STUDY OF THE EFFECT OF THIRD ELEMENTS ON DETERMINATION

OF WOLFRAM, COBALT, MOLYBDENUM, NICKEL, CHROMIUM,

MANGANESE, BORON, ALUMINUM AND COLUMBIUM IN HEAT-

RESISTANT STEELS

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A. G. Komarovskiy

The growing demand for simple and rapid physical methods for the analysis of heat-resistant steels impelled the author to work on the development of a quantitative spectrum analysis method. He attempted to realize three chief assignments: first, to develop a method which would permit determination of any content of elements in any heat-resisting steel under similar electrical conditions; secondly, to select those pairs of lines which would make possible the determination of any amount of an element by a single calibration line; thirdly, to reduce the number of standards required for plotting calibration curves for any steel, to a minimum, i.e. to one specimen. In addition, the effect of third elements was studied.

For solution of these problems, numerous alloys of binary, ternary, quaternary, quinary and still more complex systems were made covering perlitic and austenitic ranges of heat-resisting steels.

Results of the chemical analysis of cast specimens are given in Tables 1 and 2.

Spectrograph ISP-22 was used for obtaining the spectra of the samples under investigation. The spark was employed as an excitation source in determination of W, Co, Mo, Ni, Cr and Mn. Photometric evaluation was done with a micro-photometer.

Determinations of B, Al and Cb were conducted by a-c arc spectra. The micro-photometer was also used for evaluating Cb and Al lines, but the method of photometric interpolation was accepted for B.

Conditions for obtaining spark spectra were as follows: voltage in the transformer primary winding was 220 v, current amounted to 3.5 a; voltage in the secondary winding was 10,600 v (third stage of transformer); capacity of con-densers - 6,500 cm, spark gap - 2.5 mm, width of spectrograph slit - 3.5 divisions; exposure time - 60 sec; the upper electrode represented a rod of pure electrolytic copper 8-9 mm in diameter, tapered to 3-4 mm diameter.

Diapositive plates with sensitivity of 1-2° (H. and D.) were used for photo-graphs of spark spectra, being developed in metel-hydroquinone developer. During plotting of calibration diagrams, transition from blackening to relative intensity of lines was realized with the aid of the characteristic curve of the photographic plate, for which purpose one of the spectra of a sample under investigation was photographed with a step reducer.

Following were the conditions for obtaining arc spectra: current - 4a for columbium, 6-7a for boron and 7-8a for aluminum; arc gap ⊖ 3 mm; width of the slit - 2.5 divisions for columbium, 1.25 for boron and 1.5 for aluminum; burning time - 10 sec; exposure - 30 sec; other conditions were the same as those for a spark.

Analytical pairs of spectrum lines are given in Table 3.

Specimens of various heat-resisting steels were photographed, separately for each element, three times on the same plate simultaneously with the speci-mens of the corresponding binary system; this procedure was repeated on five different plates of the same lot.

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Determinations of B, Al and Cb were conducted by a-c arc spectra. The micro-photometer was also used for evaluating Cb and Al lines, but the method of photometric interpolation was accepted for B.

Conditions for obtaining spark spectra were as follows: voltage in the transformer primary winding was 220 v, current amounted to 3.5 a; voltage in the secondary winding was 10,600 v (third stage of transformer); capacity of condensers - 6,500 cm, spark gap - 2.5 mm, width of spectrograph slit - 3.5 divisions; exposure time - 60 sec; the upper electrode represented a rod of pure electrolytic copper 8-9 mm in diameter, tapered to 3-4 mm diameter.

Diapositive plates with sensitivity of 1-2° (H. and D.) were used for photographs of spark spectra, being developed in metal-hydroquinone developer. During plotting of calibration diagrams, transition from blackening to relative intensity of lines was realized with the aid of the characteristic curve of the photographic plate, for which purpose one of the spectra of a sample under investigation was photographed with a step reducer.

Following were the conditions for obtaining arc spectra: current - 4a for columbium, 6-7a for boron and 7-8a for aluminum; arc gap - 3 mm; width of the slit - 2.5 divisions for columbium, 1.25 for boron and 1.5 for aluminum; burning time - 10 sec; exposure - 30 sec; other conditions were the same as those for a spark.

Analytical pairs of spectrum lines are given in Table 3.

Specimens of various heat-resisting steels were photographed, separately for each element, three times on the same plate simultaneously with the specimens of the corresponding binary system; this procedure was repeated on five different plates of the same lot.

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Calibration diagrams, plotted according to averaged results of photometric evaluation, are presented in Figure 1-9. Each point on the curves represents an average value from 15 spectrograms.

Figure 1 contains calibration curves for wolfram.

Curve I is plotted according to specimens No 1-4 of a binary system (numeration everywhere corresponds to the numeration of specimens in Tables 1 and 2); curve II is constructed by data obtained for specimens N6. 49-51.

Figure 2 refers to cobalt. Curve I is constructed by specimens No 5-10 of a binary system, curve II - by specimen No 60, curve III - by specimens No 56-59, curve IV - by No 52-55.

Table 1

Average Chemical Composition of Binary Alloys

Nos of Alloys	System Designation	C	Si	W	Co	Mo	Ni	Cr	Mn*

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Table 1

Average Chemical Composition of Binary Alloys

Nos of Alloys	System Designation	Composition										
		C	Si	W	Co	Mo	Ni	Cr	Mn*	B	Al	Cb
1	Iron-Wolfram	0.06	Trace	2.65								
2		0.04	"	6.30								
3		0.08	"	8.45								
4		0.04	"	17.35								
5	Iron-Cobalt	0.025	0.06	-	4.29							
6		0.030	0.05	-	10.68							
7		0.030	0.08	-	17.20							
8		0.030	0.05	-	22.28							
9	0.030	0.030	0.10	-	28.32							
10		0.020	0.07	-	48.40							
11	Iron-Molybdenum	0.22	0.37	-	0.34	0.34						
12		0.24	0.32	-	0.75	0.75						
13		0.20	0.35	-	1.25	1.25						
14		0.33	0.29	-	-	1.59						
15		0.34	0.30	-	-	1.75						
16		0.49	0.33	-	-	2.00						
17		0.29	0.31	-	-	2.50						
18		0.36	0.38	-	-	4.38						
19	Iron-Nickel	0.27	0.23	-	-	-	5.16					
20		0.30	0.28	-	-	-	10.28					
21		0.28	0.20	-	-	-	14.84					
22		0.45	0.22	-	-	-	29.45					
23		0.66	0.27	-	-	-	39.68					
24		0.75	0.24	-	-	-	55.00					

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Nos of Alloys	System Designation	C	St	W	Composition			Cr	Mn*	B	Al	Cb
					Co	Mo	Ni					
25	Iron-Chromium	0.14	0.32					0.34				
26		0.19	0.35					0.48				
27		0.14	0.28					0.90				
28		0.20	0.23					2.34				
29		0.19	0.39					5.07				
30		0.18	0.50					9.50				
31		0.11	0.72					24.40				
32	Iron-Manganese	0.33	0.23						0.48			
33		0.56	0.70						2.39			
34		1.15	0.93						8.09			
35		2.39	1.15						27.88			
36	Iron-Boron	0.23	0.41							0.003		
37		0.24	0.37							0.085		
38	Iron-Aluminum	0.23	0.49								0.015	
39		0.18	0.53								0.10	
40		0.21	0.46								0.38	
41		0.19	0.45								1.53	
42	Iron-Columbium	0.29	0.37									0.10
43		0.26	0.36									0.37
44		0.32	0.40									0.77
45		0.25	0.33									0.92
46		0.30	0.44									1.35
47		0.27	0.41									1.78
48		0.29	0.38									3.16

*The manganese content in other systems of this table is 0.3-0.4%.

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Average Chemical Composition of Heat-Resisting Alloys and Complex Alloy Steels

Table 2.
Таблица 2

Средний химический состав жаропрочных сплавов и сложных легированных сталей

No.	C	Si	Mn	Cr	Ni	Mo	W	V	Co	Ti	Al	B	Cb
49	0,08	0,05	0,17			3,40	2,73						
50	0,06	0,08	0,12			3,60	11,98						
51	0,06	0,05	0,06			3,70	24,81						
52	0,12	0,98	0,97	17,0	3,00				2,50				
53	0,14	1,08	1,80	15,40	10,35				7,67				
54	0,16	1,28	0,18	16,25	38,80				20,36				
55	0,28	0,95	0,37	20,60	30,26				36,79				
56	0,30	0,70	0,41	17,25	15,87		2,46		2,58	0,25			
57	0,30	0,97	0,39	14,06	15,70		0,74		2,98	0,44			
58	0,22	1,16	0,40	17,35	16,81		4,59		3,60	0,27			
59	0,05	0,81	0,58	16,51	17,60		3,47		5,85	0,51			
60	0,56	0,84	0,78	13,06	12,56	2,25	3,21		9,01	0,12			
61	0,49	0,70	1,41	15,40	24,11	6,80							←1,10
62	0,54	0,52	0,68	16,15	23,82	5,25							
63	1,17	0,65	0,55	7,18	7,68	0,37	2,70						
64	0,64	0,90	0,87	11,19	15,80	4,04	3,67						
65	1,31	1,98	7,42	14,10	6,49	1,20		1,26					
66	1,10	1,47	5,58	17,11	8,80	0,90		1,34					
67	0,70	0,67	0,65	5,65	9,11	0,61	3,42						
68	2,11	1,09	6,27	16,89	7,15	1,78		1,14					
69	0,69	0,29	0,68	2,56	Пот	0,21	2,48	1,14					
70	0,71	0,05	0,36	6,49	»	1,20	4,00	0,57					
71	0,68	0,05	0,46	3,55	»	0,88	23,66	0,62					
72	0,69	0,25	0,70	6,90	»	0,77	20,50	1,52					
73	0,75	0,25	0,68	7,01	»	2,50	21,20	1,51					
74	0,80	0,30	0,47	2,77	»	0,36	12,18	0,52					
75	0,50	0,61	2,11	13,92	21,72	0,52							
76	0,45	0,89	0,71	15,90	12,65								
77	0,11	0,65	0,40	24,5	20,00								
78	0,11	0,80	0,63	15,50	20,17								
79	2,49	1,41	6,21	16,82	8,71	1,56							
80	1,03	1,75	5,15	15,08	10,08	9,11							
81	0,70	0,94	0,99	14,19	11,05	1,90		67	1,26				
82	0,68	0,75	1,25	15,25	23,08	6,46							
83	1,00	0,40	0,41	8,30	10,85	Сталь	0,33						
84	0,42	0,85	2,11	14,1	22,31	6,66							
85	1,67	0,79	0,44	12,62	11,55	1,00	2,50						
86	2,25	1,29	6,45	17,00	6,82	1,57		1,60					
87	0,95	0,62	0,40	4,90	7,05	0,26	2,55						
88	0,80	0,35	0,20	8,00		1,10	1,00	0,40					
89	0,74	0,07	0,46	5,33		1,26	9,66	0,57					
90	0,75	0,29	0,35	5,00		0,72	17,01	0,57					
91	0,79	0,37	0,45	1,00		1,00	18,34	0,69					
92	0,57	0,61	8,66		8,25	Сталь	0,80	0,35					
93	0,11	0,90	0,63	15,5	20,0						0,025		
94	0,11	0,90	0,63	15,5	20,0						0,080		
95	0,15	0,65	0,40	24,5	20,0						0,080		
96	0,15	0,60	0,55		0,78						0,025		
97	0,15	0,60	0,55		0,78						0,16		
98	1,24	0,64	12,75								0,065		
99	1,24	0,46	12,75								0,12		
100	0,10	0,36	0,48	14,94	25,46						0,021		
101	0,10	0,36	0,48	14,94	25,46						0,083		
102	0,10	0,36	0,48	14,94	25,46						0,20		
103	0,10	0,36	0,48	14,94	25,46						0,38		
104	0,10	0,36	0,48	14,94	25,46						1,48		
105	0,08	1,19	0,61	16,39	75,21				3,51	0,16			0,10
106	0,04	1,91	0,68	18,15	72,31				3,46	0,60			0,23

Изучение влияния третьих элементов на упрочнение W, Co, Mo, Ni   575

Average Chemical Composition of Heat-Resisting Alloys and Complex Alloy Steels

№ п/п	C	Si	Mn	Cr	Ni	Mo	W	V	Co	Ti	Al	B	Nb	Cu
107	0,04	1,18	1,42	14,80	75,08					4,19	1,81	—		0,42
108	0,21	0,46	0,42	12,00	14,81								0,15	
109	0,19	0,39	0,48	11,57	15,16								0,45	
110	0,23	0,43	0,39	10,98	14,75								1,20	
111	0,20	0,40	0,44	11,81	15,09								1,50	
112	0,11	0,81	0,83	15,30	12,11	1,18								
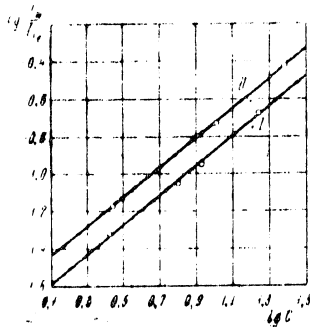
Figure 1.
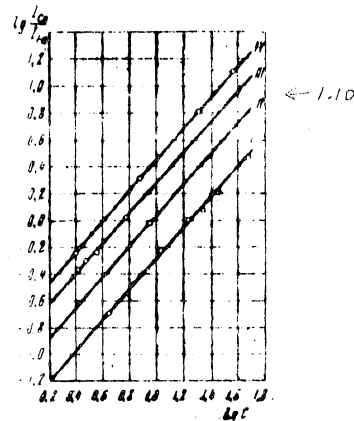
Figure 2.
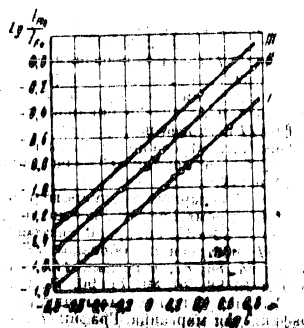
Figure 3.
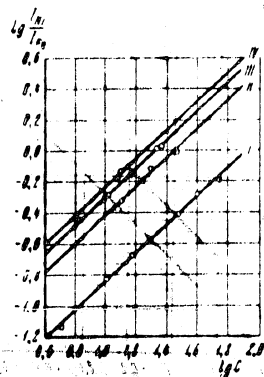
Figure 4.

Figure 3 gives calibration curves for molybdenum. The curve I is plotted for alloys Nos 11-18 of a binary system, curve II - for specimens No 61-68 and curve III - for specimens No 69-73.

Figure 4 presents calibration curves for nickel: I corresponds to alloys No 19-24 of binary system, II - to specimens No 76-78, III - to specimens No 79, 80, 81, 75, 82 and IV - to specimens No 60 and 112.

Figure 5 contains curves for chromium: I - for alloys No 25-31, II - for specimens No 83, 84, 63, 85, 64, 86, 87, and III - for specimens No 88, 70, 89, 74, 90, 71, 91.

Figure 6 shows calibration curves for manganese. Curve I is plotted by results obtained from alloys No 32-35, curve II - is plotted by specimens No 83, 84, 61, 64, 86, 66, 92 and curve III - by No 70-73.

Figure 7 gives curves for boron. Curve I is constructed by alloys No 36 and 37 of a binary system, curve II - by No 93 and 94, curve III - by No 96 and 97 and curve iv - by specimens No 98 and 99.

Figure 8 presents calibration curves for aluminum. Curve I corresponds to alloys No 38-41 of a binary system, curve II corresponds to specimens No 100-104 and III - to No 105-107.

Figure 9 deals with columbium. Calibration curve I is plotted by data from alloys No 42-48 and curve II - by results obtained from No 108-111.

Figure 1-9 show that the calibration curves of complex alloys are shifted into positions strictly parallel to the calibration curves of binary alloys. This displacement is conditioned by increase in the intensity of lines of an admixture to be determined due to presence of the third elements, which factor is illustrated by data given in Table 4 where each number is an average value taken from 9 photographs.

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Table 3

Analytical Pairs of Spectrum Lines

| Element to be Determined | Wavelengths (A) | | Concentration |
	Element to be Determined	Elements for Comparison, Fe	Range (%)
Wolfram	2488.77	2413.31	0.9 30.0
Cobalt	2414.46	2422.68	0.7 48.0
Molybdenum	2775.40	2776.18	0.1 8.0
Nickel	2992.60	3000.95	5.0 55.0
Chromium	3128.70	3167.86	0.3 25.0
Manganese	2933.06	2730.74	0.3 30.0
Boron	2496.78	2493.26	0.002 0.2
Aluminum	3082.16	3055.26	0.015 1.5
Columbium	3130.79	3083.74	0.1 4.0

Table 4

Dependence of the Intensity of Manganese Lines on Presence of Third Elements in Alloy

No of Specimens	System of Alloy	Mn Content, %	$\lg I_{Mn}$	$\lg I_{Fe}$	$\lg \dfrac{I_{Mn}}{I_{Fe}}$
32	Iron-Manganese	0.48	0.03	1.69	−0.66
74	High-Alloy Steel	0.47	1.38	1.72	−0.34
33	Iron-Manganese	2.39	1.69	1.75	−0.06
75	High-Alloy Steel	2.11	1.93	1.71	−0.22

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This table shows that the ratio of line intensities $\lg\frac{I_{Mn}}{I_{Fe}}$ in specimens of steels of two systems (iron-manganese and high-alloy steels) with approximately similar manganese content is essentially different. The intensity of manganese lines in specimens of high-alloy steels is considerably higher than in steel specimens of the iron-manganese system. This factor causes a parallel shift of calibration curves.

Numerous determinations of W, Co, Mo, Ni, Cr, Mn, B, Al and Cb in various heat-resisting alloys and complex alloy steels, conducted by calibration lines I, II, III and IV of Figure 1-9, led to the following conclusions: correct results of determination may be obtained by calibration line II of Figure 1 for wolfram in specimens containing 1.5-24% W and 3.5-4.5% Mo; specimens which contain only insignificant quantities of other admixtures in addition to wolfram, may be analyzed correctly by calibration curve I of Figure 1.

Correct results are obtainable by calibration curve IV of Figure 2 for determination of cobalt in steels containing 2-37% Co, 15-20% Cr and 10-29% Ni, curve III is adaptable for analysis of specimens containing cobalt in 2-6% range, chromium in 14-18% range, 15 to 18% nickel 0.2 to 0.6% titanium; specimens containing about 9% Co and approximately 13% Cr, 13% Ni, 2% Mn, 0.2% Ti and 1% Cb, have to be analyzed by calibration curve II of Figure 2. Alloys containing only cobalt and small amounts of other additions, are analyzed by curve I of Figure 2.

Determination of molybdenum in steels, containing molybdenum in 0.2-2.5% range, 2-7% Cr, 2-23% W and 0.5-1.5% V, is conducted by calibration curve III of Figure 3; for specimens containing 0.3-6.8% Mo, 5-17% Cr, 6-24% Ni, 2-3.5% W, 0.5-1.5% V and 0.4-7% Mn, calibration curve II of Figure 3 is adaptable.

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Determination of nickel in steel containing, in addition to nickel, 13-17% Cr, 1.0-2.5% Mo, 3-4% W, 1-9% Co, 0.12-0.8% Ti and 0.8-1.5% Cb, is conducted by calibration curve IV of Figure 4; curve III of Figure 4 must be used for analysis of steels with 12-30% Ni, 9-17% Cr, 0.3-6.5% Mo, 3-6% W and 0.2-1.5% V; specimens containing, besides nickel, only chromium in 15-25% range have to be analyzed by curve II of Figure 4.

Determination of chromium within 0.3-30% range and only a small percentage of other alloying elements, is conducted by calibration curve I of Figure 5; curve II of Figure 5 must be used for specimens containing, in addition to chromium, 0.4-7% Mn, 6-22% Ni, 2-7% Mo, 0.2-6% W, 0.2-2% V, 0.2-1.5% Si and 0.2-2.5% C; calibration curve III of Figure 5 gives good results in determination of chromium in steels which, in the complete absence of nickel, contain alloying elements in the following ranges: 1.6-8% Cr, 1-23% W, 0.4-1.5% V, 0.2-1.26% Mo.

Determination of manganese in the samples of steels containing, in addition to manganese, 2-7% Cr, 4-21% W, 0.2-1.5% Mo, is conducted by curve III of Figure 6; steels, containing manganese within the 0.3-8.6% range, 6.0-25.0 Ni, 0.5-17% Cr, 0.9-7% W, 0.2-7% Mo, 0.2-1.6% V, 0.6-1.5% Si and 0.4-2.25% C, are analyzed by curve II; calibration curve I of Figure 6 gives correct results for steels which contain, besides manganese, only nickel up to 9%.

Determination of boron in steels containing, in addition to boron, 15.5-24.5% Cr and 13-20% Ni, may be conducted by calibration curve II of Figure 7; specimens containing, in addition to boron, 0.55-1% Mo and 0.78-1.5% Ni, are analyzed by curve III; specimens, containing boron within the range from 0.0065 to 0.12% and 12-13% Mn, correspond to curve IV of Figure 7.

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Analysis of aluminum in steels, containing, in addition to aluminum, 14-
19% Cr, 72-75% Ni and 3-4% Ti is conducted by calibration curve III of Figure 8;
specimens with aluminum within the 0.02-1.5% range, containing 14-15% Cr and
25-26% Ni have to be analyzed by curve II of Figure 8.

Determination of columbium in steels, containing, in addition to columbium,
8-15% Cr and 9-16% Ni, is conducted by calibration curve II of Figure 9.

Determination of elements by a calibration curve, which does not correspond
to a given type of steel, may result in an error of up to 250%.

The accuracy in determination of elements, using proper calibration curves,
is as follows: $\pm$ 2.4% for wolfram, $\pm$ 3% for cobalt, $\pm$ 2.2% for molybdenum (at
2.5% concentration), $\pm$ 2.9% for nickel, $\pm$ 2.1% for chromium (at 12% concentration),
$\pm$ 2.1% for manganese (at concentration of 10%), $\pm$ 2.8% for boron, $\pm$ 3.3% for
aluminum and $\pm$ 2.0% for columbium.

The regularity established for the parallel shift of the calibration curves
for various heat-resisting alloys and complex alloy steels in respect to the
calibration curves of binary systems has great practical significance, since
it permits a considerable decrease in the number of standards required for
plotting calibration curves. If the value of parallel shift $\Delta lg \frac{I_{limit}}{I_{average}}$

is known for a certain type of alloy or steel in respect to the calibration
curve of a binary system, a parallel curve may always be plotted without stan-
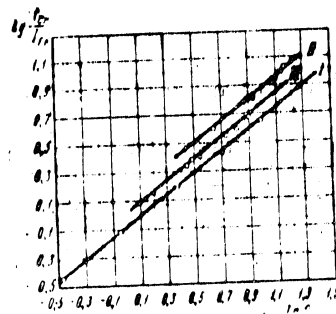dard specimens or, at least, by the point of a single standard *specimen.*
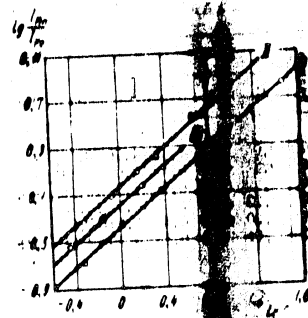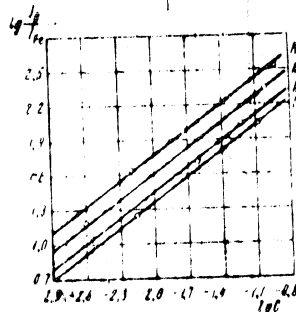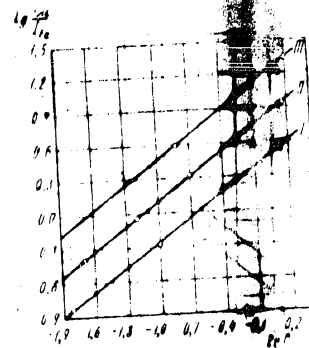
- 10 -
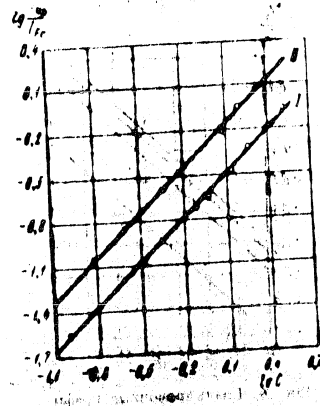
Figure 5.

Figure 6.

Figure 7.

Figure 8.

Рис. 3 содержит градуировочные графики для молибдена. График I построен по образцам № 11—18 бинарной системы; график II построен по образцам № 61—66, а график III — по образцам № 69—73.

На рис. 4 приведены градуировочные графики для никеля. График I построен по образцам № 19—24 бинарной системы, график II построен по образцам № 76—78, график III построен по образцам № 79, 80, 81, 75, 82, а график IV — по образцам № 60 и 112.

Рис. 5 содержит градуировочные графики для хрома. График I построен по образцам № 25—31 бинарной системы, график II построен по образцам № 83, 85, 64, 86, 87, а график III — по образцам № 68, 70, 89, 74, 90, 73, 91.

На рис. 6 приведены градуировочные графики для марганца. График I построен по образцам № 52—55 бинарной системы,

Figure 9.